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MERCURY POLLUTION CONTROL IN STREAM AND LAKE SEDIMENTS

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16. Abstract

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Long-term evaluation of mercury getter systems indicates that pH and dissolved oxygen are important only to the extent that they affect the concentration of desorbed mercury in the vicinity of the getter. (Lowry-Texas)

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This report was submitted in fulfillment of Project Number 16080 HTD, Contract 68-01-0086, under the sponsorship of the Environmental Protection Agency.

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SECTION I

CONCLUSIONS

1. Sulfur coated cotton meshwork (net) will remove inorganic mercury from contaminated water and sediments. The rate of removal is proportional to the contamination level and the partition coefficient between the dissolved mercury and absorbed mercury. This system is most effective in anaerobic sediments.

2. Polyvinyl alcohol gel containing sulfur or phenyl thiourea will rapidly remove inorganic mercury from highly contaminated water and sediments but is generally not applicable to sediment contamination levels below about 25 to 50 ppm or where the getter must be deployed for long time intervals.

3. Methyl mercuric chloride can be gettered by phenyl thiourea dispersed in polyvinyl alcohol gel.

4. Metallic mercury can be quickly and irreversibly removed by elemental sulfur at a rate proportional to the surface area of the getter.

SECTION II

RECOMMENDATIONS

1. A sulfur coated cotton mesh should be constructed and deployed at an early date to test its effectiveness under actual field conditions.

2. The development of a stable coagulated polymer gel system as a "methyl mercury" getter should be pursued in order to prepare a recoverable mesh for field testing.

3. Consideration should be given to further study of the plating out of mercury on cleaned plastic surfaces and the competitive aspects of this with other short-term regenerable getter systems.

4. Further research should be conducted to determine the economic feasibility of recovering mercury from the getter system once it has been removed from the sediment.

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SECTION III

INTRODUCTION

Mercury contamination enters streams and lakes from a variety of sources. It becomes sorbed onto the sediments where it resides in dynamic equilibrium with the dissolved species in the suprajacent water column. Aquatic biota may then ingest mercury and become contaminated. As mercury accumulates throughout the food web, it concentrates in higher life forms and ultimately in man. Even if the discharge of mercury could be completely halted, its presence in fluvial and estuarine sediments still poses a potential threat of considerable magnitude. The reliance on natural dispersive mechanisms to dilute and eliminate mercury pollution is no longer tenable as evidenced by high mercury levels in tuna and swordfish. Selected species of edible fin and shell fish have been withdrawn from the market causing economic hardship in many coastal areas dependent on fishing for a livelihood. It is therefore evident that means must be found to remove mercury from sediments without destroying the environment or otherwise upsetting the ecological balance.

Under anaerobic conditions frequently found in stream and lake bed sediments, mercury in the presence of sulfur may be precipitated as mercuric sulfide. This reaction was verified under laboratory conditions prior to initiation of this project and found to be effective as a means of removing mercury from contaminated waters.

The problem of mercury immobilization and removal was addressed by evaluating a number of recoverable sulfur based getter systems. Examples of these are: (1) elemental sulfur deployed as a coating on a recoverable meshwork, and (2) thiourea type organic compounds dispersed in a recoverable matrix. In the course of these evaluations several improved getter system combinations became obvious and these were also included into the scope of this research.

During this project, only natural sediments and waters were used to prepare test aquaria in order to simulate natural conditions as nearly as possible. The choice was indeed fortunate because it was found that the behavior of mercury in nature is more complicated than theory would indicate. The difficulty arises because of the affinity of humic materials for mercury. This investigation further revealed that many high molecular weight natural products absorb mercury. Consequently, this project required more fundamental research than was originally planned on techniques to desorb or break the humic mercury complexes and make the metal available to the getter. The results presented herein are based on approximately 2000 mercury analyses covering a wide variety of getter combinations and environmental conditions.

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The getter systems were evaluated with respect to their ability to remove metallic mercury, the mercuric ion and organometallic species from both sand and silt-clay type sediments. Each getter was tested under pH conditions ranging from pH 5 to 9. Oxygen content in the aquaria was varied from aerobic to anaerobic.

SECTION IV

METHOD OF STUDY

Laboratory Equipment

In order to insure against any extraneous mercury contamination during this study, the entire laboratory was thoroughly cleaned prior to initiation of any experimentation. All mercury thermometers and mercury containing compounds were removed. The floor was cleaned with Mercury X, a commercial mercury scavenger. Also, all sink drains were removed and cleaned.

Only borosilicate glassware, polyethylene, and polypropylene bottles were used during the course of this project. All containers were new when the project was initiated. Each container, prior to use, was cleaned with mercury-free materials by the following procedure:

1. Washed with hot soapy water.
2. Rinsed thoroughly with hot tap water.
3. Rinsed with distilled water.
4. Rinsed with 50% concentrated nitric acid.
5. Rinsed with distilled water.

Following Step 5 each bottle was sealed and placed in a closed cabinet until needed.

Test Aquaria

In order to rapidly determine which of the four proposed mercury getter systems would offer the broadest range of applicability under varying environmental conditions a series of tests were devised to provide a quick look at each system.

For each of the four getter systems eighteen one liter polyethylene aquaria were established. Each group consisted of three sets of six aquaria each at pH 5, 7, and 9, respectively. Within each pH group there were 2 samples under anaerobic conditions, 2 samples under aerobic conditions, and two controls. Nine of the 18 were devoted to silt-clay

type sediment and nine aquaria contained quartz sand. All experiments were conducted at room temperature (21 to 23°C).

Sediments

Two sediment types were selected to simulate sediment conditions that might be encountered in nature. First, a silt-clay type sediment was collected from under approximately 2 feet of water at Lake Arlington, Tarrant County, Texas. This material was wet sieved through a U.S. Standard 200 mesh screen primarily to remove the coarser organic material. The fraction finer than 74 microns which was used for establishing the test aquaria consisted predominantly of quartz with approximately 28% calcium carbonate and 3% organic matter. Second, a medium grain, well sorted, iron stained, quartz sand was collected along the south shore line water level of Cedar Creek Lake, Henderson County, Texas. This material contained neither carbonate nor organic fractions.

The original proposal stated that Ottawa sand would be used. However, it was subsequently decided that it was unlikely that material of this purity would be encountered in any contaminated natural environment. Mercury determinations were performed on all sediment batches before use in the aquaria.

Water

During the course of this project all mercury solutions used for inoculating the test aquaria were made with water from Lake Arlington, Tarrant County, Texas. Repeated analysis of Lake Arlington water revealed a background mercury concentration of 0.004 ppm. Viable microorganisms were present in the water. Though valuable in the attempt to simulate field conditions, these organisms did tend to complicate the interpretation of the early data.

Proposed Getter Systems

The basic getter systems to be evaluated were fiber or steel meshworks coated with:

a. elemental sulfur; or
b. paraffin doped with sulfur; or
c. parafin doped with a thio-organic such as thiourea; or
d. polyvinyl alcohol polymer gel, acidified, coagulated and doped with elemental sulfur.

In addition certain other combinations of these were investigated as getter systems.

Analytical Procedure

Mercury analyses in this project were performed following a reduction-aeration technique essentially the same as the Hatch and Ott (1968) method. This technique consists of oxidizing the sample to form the mercuric ion using excess potassium permanganate in a nitric acid-sulfuric acid solution followed by reduction to the metallic state by stannous chloride solution. The sample is connected to an aerator which vaporizes the mercury and pumps these vapors through a UV absorption cell. A 2537 Å line emitted by a mercury lamp is absorbed by the vapor in proportion to the mercury concentration and the results are read directly on the instrument meter. Only mercury-free reagents are used in this process.

A Coleman Instrument Company Model MAS-50 mercury analyzer system was used for in-house analysis. The instrument was calibrated with standard solutions of known concentration prior to each day's use and the calibration was checked periodically during each day's use. A Perkin-Elmer Model 303 atomic absorption unit was used for all sub-contract analyses.

Water analyses using the MAS-50 instrument are straightforward but the instrument has a saturation limit of 9 micrograms of mercury in the sample volume to be analyzed. The technique uses 100 ml of an aqueous sample for analysis. Lower volumes of high mercury content solutions are appropriately diluted to keep the meter reading on scale. Sediments and other mercury-containing solids require vigorous digestion procedures with strong oxidants. The more tightly-bound mercury samples require higher concentrations of oxidants and longer digestion periods. Incomplete digestion may result in erroneous readings. These may be reflected by low readings where the incomplete digestion has left the mercury bound to its sorbent. Conversely, erroneously high readings can be obtained from incompletely digested materials whose vapors can also absorb 2537 Å radiation such as oxides of sulfur and nitrogen. Sediment analysis are accurate to within 10%, based on verification by subcontracted analyses.

Digestion Procedure

Procedures for digesting mercury-contaminated sediments vary with sediment type and organic content. High organic levels necessitate the use of high acidity oxidizing agents. Basically, the procedure is one of first using stronger oxidants to destroy any organic matter

and then weaker oxidants to preserve the oxidized character of the digestion products until the sample can be analyzed. All samples are carefully ground and normally a one gram sample is used for digestion. A condensor is installed in the digestion flask and used throughout the procedure with reagents being added through the condensor to eliminate any mercury loss.

Procedure

(1) Slowly grind sediment sample in an agate mortar.

(2) Weigh out 1 gm sample and place in digestion flask.

(3) Add:
    (a) 10 ml concentrated H_2SO_4;
    (b) 10 ml H_2O_2.

(4) Digest at 100°C for 20-30 minutes.

(5) Add:
    (a) 10 drops of potassium permanganate (4%);
    (b) 5 ml of 5% potassium persulfate solution.

(6) Continue digestion at 100°C for 1 hour.

(7) Cool, remove condenser and dilute entire sample to 250 ml and make Hg determination.

The concentration of mercury present in sediment samples may be calculated by the following method:

$$\frac{(\text{micrograms measured mercury}) \times (250 \text{ ml})}{(\text{grams sediment}) \times (\text{ml analyzed sample})} = \text{ppm}$$

Disposal of Mercury Contaminated Laboratory Wastes

All waste materials resulting from these experiments were considered as toxic materials and were turned over to the LTV Aerospace Corporation Safety Officer for disposal.

SECTION V

BEHAVIOR OF MERCURY IN WATER AND SEDIMENTS

Three forms of mercury contamination were studied: 1. the free metal; 2. mercuric ion; and, 3. organometallic species. Of these, the organic form constitutes the greatest hazard. A study of the behavior or each mercury form in a simulated natural sediment-water environment was conducted to aid in selecting the optimum getter system.

Bulk mercury metal dumped into the environment usually filters through the porous sediments as far away from the sediment-water interface as the soil conditions will allow. Once diffusion is beyond a few inches, the metal is immobilized and out of the normal zone of biological activity. Metallic mercury has low solubility in water (less than 1 ppm as Hg°) and, unless present in large quantities such as from placer gold mining spills, it is not exposed and contributes little to the problem of contaminated waters. However, colloidal mercury formed by reduction of ionic species does contribute heavily to the problem of contaminated sediments. Whenever oxidizing conditions are present, the free metal can be converted to the more soluble ionic form which is free to migrate, thus increasing the zone of contamination. The reduced metallic mercury acts as a concentrated "in situ" source of more lethal mercury forms.

Behavior of the mercuric ion (Hg^{++}) in natural waters is strongly dependent upon the nature of the sediments and secondarily on pH, dissolved oxygen content and redox conditions. Since Jernelöv (1971) and Hem (1970) have discussed these conditions, a detailed description is not considered necessary here. Still, several points should be discussed as they relate to both design and operational effectiveness of any mercury getter system.

High levels of mercuric ion contamination usually do not exist in natural waters. The ion adsorbs to sediments and for any particular sediment type, there is a family of water-sediment mercury equilibrium curves whose break point varies with humic fraction and grain size (Figure 1). In addition, the mercuric ion chemisorbs to humic materials to form strong complexes; thus, there results a competitive natural gettering action by the sediments (Figure 2). When these localized organic complexes are broken, mercury will be released either as the mercuric ion or as lower molecular weight, often soluble, humic fragments free to redistribute the contamination. Jernelöv (1969, 1971) has reported that bacteria will convert the mercuric ion to methylated species but the fate of the soluble complex forms is still open to question. Based on these factors, it is obvious that environmental improvement can be achieved by either removing all the mercury or by at least gettering the mercuric ion from which the highly toxic methylated mercury species are formed.

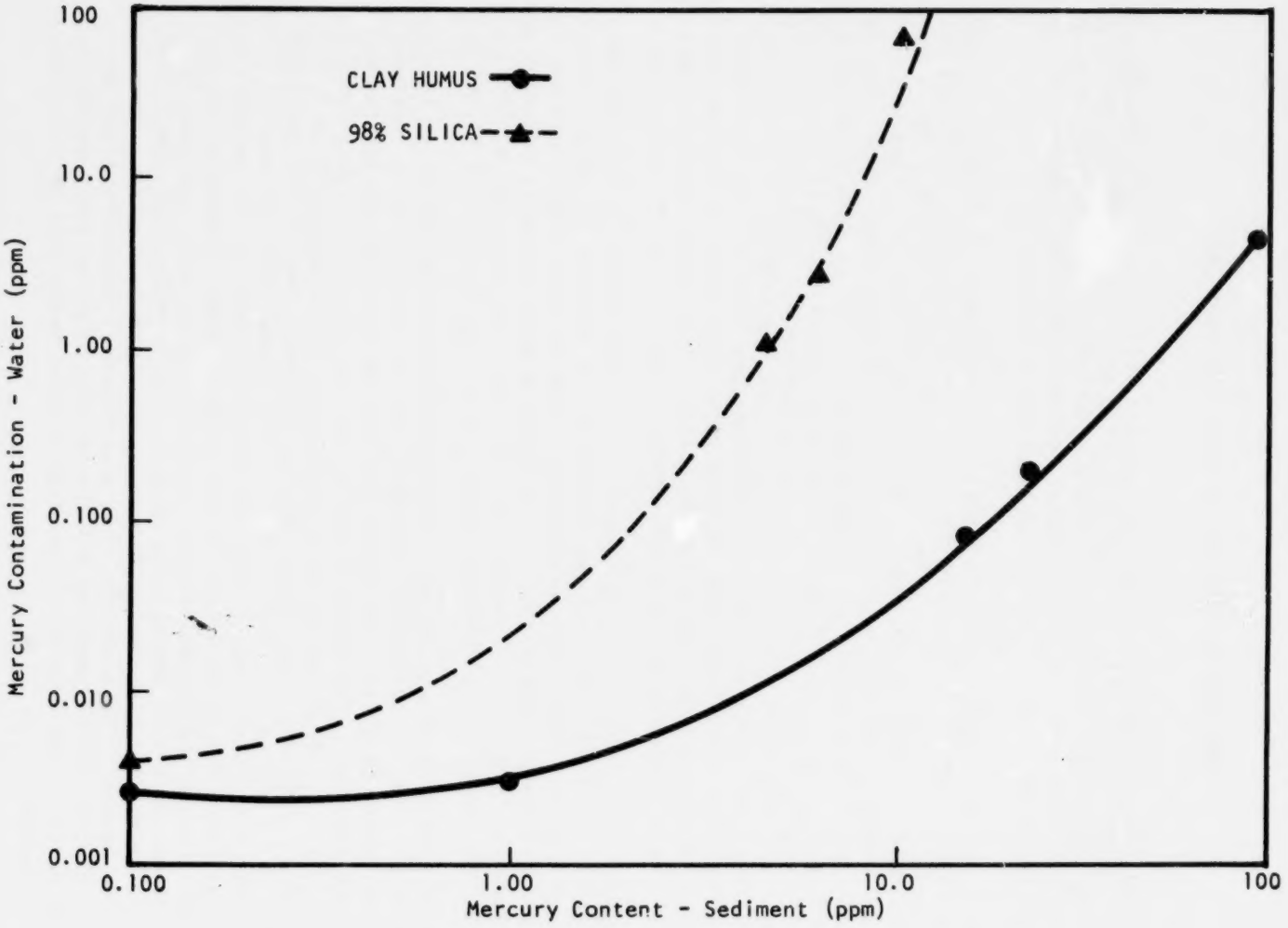

FIGURE 1 MERCURY EQUILIBRIA BETWEEN WATER AND SEDIMENTS

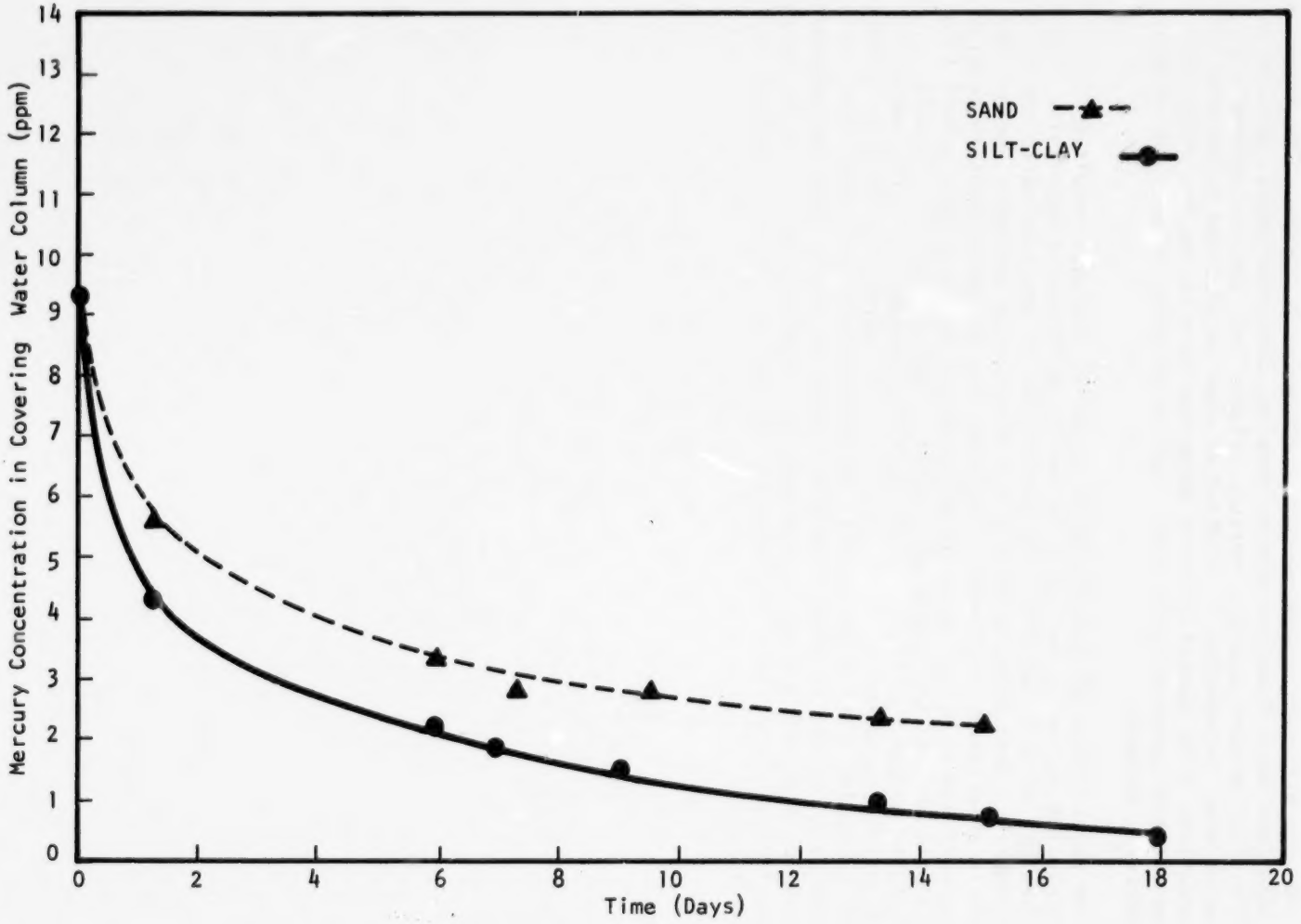

FIGURE 2 ADSORPTION OF MERCURY ION BY NATURALLY OCCURRING SEDIMENTS

Two very different organo-mercury forms exist in nature. The first, a localized humic fraction mercury complex, described above, acts as an "in situ" mercury source. Mercury release into the environment will occur when the complex is oxidized or when metabolized by benthic organisms. The second and more dangerous form is the low molecular weight true organometallic form such as dimethyl mercury or phenyl mercuric acetate.

The exact nature of the alkylated mercurial products resulting from bacterial action on the mercuric ion in sediments is uncertain. Usually, dimethyl mercury and methyl mercuric chloride are considered the primary products. When humic materials are absent from sediments, methyl mercuric chloride moves freely. Even when the sediments contain several percent humus, methyl mercuric chloride was found to have a half life of 6-10 days in the suprajacent water column (Figure 3). Similarly, soluble mercury complexes resulting from breakdown of humic sediment fractions, move freely in the water but the mercury is usually released or exchanged to stronger bonding sediment adsorption sites. Obviously, complete removal of organic mercury compounds would solve the contamination problem. Practically, prevention of their formation in the aquatic environment would help to reduce the ecological impact of mercury contamination.

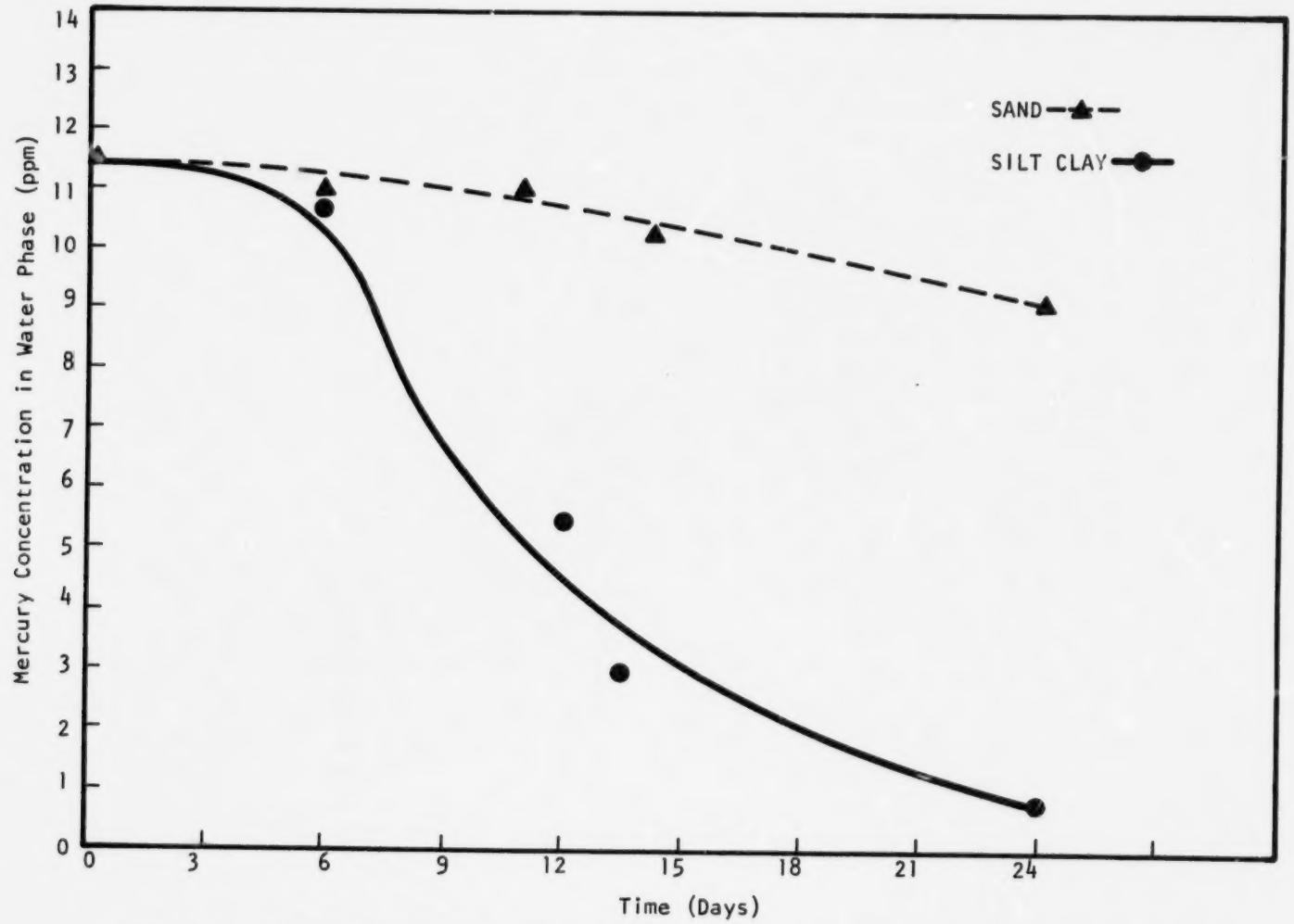

FIGURE 3 LIFETIME OF METHYL MERCURIC CHLORIDE IN SIMULATED NATURAL WATER CONDITIONS

SECTION VI

DISCUSSION OF GETTER SYSTEMS

Mode of Operation

Mercury may be introduced into waterways both as soluble and as particulate forms. Soluble mercury in the fluvial environment is usually transformed to the particulate form by reduction to metallic mercury, by precipitation as sulfides or oxides, by sorption onto sediments, by complexation with nonviable particulate organics or by assimilation by viable biota (Heide 1956, Dall'Aglio 1968, and Ross 1962). Fine-grained stream sediments remove a high percentage of any slugs of mercury introduced into streams, often within a distance of a few miles of the outfall. This depends, of course, upon stream discharge, and the physical-chemical nature of the sediment. Such contaminated sediments may then be transported downstream by currents in a process that involves multiple cycles of deposition and erosion. When a river flows into a standing body of water, the coarse size and high specific gravity minerals quickly settle as a function of decreasing inflow velocity. The finer size material, which has been found to contain most of the mercury contamination, is carried in suspension or as a colloidal form and is dispersed throughout the lake in response to the prevailing circulation until it slowly settles to form the lake-bed sediment surface. Any mercury accumulated in the sediments will be reintroduced into the suprajacent water column through the natural sediment-mercury-water equilibria (Figure 1). Higher mercury level sediments induce greater mercury contamination in the overlying waters.

The mode of operation of each mercury getter system studied was found to be the extraction of that portion of the mercury contamination which was recycled into the covering water column. Getters covered by contaminated sediments perform better because there is less influence of stream currents carrying the dissolved mercury away from the zone of gettering activity. The pH and dissolved oxygen content of the water appear to affect the gettering rate only to the extent that their alteration might vary the concentration of desorbed mercury in the vicinity of the getter.

Sulfur Mesh Getter Systems

Under anaerobic conditions often found in bottom sediments, dissolved mercury precipitates as an insoluble sulfide by reacting with the sulfide ion formed "in situ" (Hem, 1970). Advanced Technology Center, Inc. has found that by using this same reaction on recoverable sulfur coated substrates mercury can be removed from contaminated waters and sediments.

Several different approaches to the deployment of elemental sulfur in water and sediments were investigated. These included recoverable: (1) high density sulfur pellets; (2) low density, high porosity sulfur melts; (3) dispersions of sulfur in recoverable matrices; and (4) high-surface area sulfur coated cotton mesh. High density pellets offered the best handling characteristics but suffered a low surface area to weight ratio. Sulfur melt preparations were effective but their friable character resulted in high sulfur losses unless handling was done with extreme care. Dispersions in polyvinyl alcohol were not stable. Coating a cotton mesh with sulfur proved the most successful approach both from the standpoint of deployment and from the efficiency of mercury removal.

Of the meshworks tested, only cotton was successfully coated. Sulfur coatings on plastic and metallic materials exhibited poor bonding properties and were not suitable for handling. Three methods of coating the mesh were studied. First, attempts were made to coat with a sulfur melt. This method was not successful as the sulfur wetted the mesh with difficulty; the resulting coating was so fragile that considerable sulfur was lost during handling. Quenching in order to achieve the so called "rubbery sulfur" did not result in any significant improvement. Coating the mesh with sulfur dispersed in melted paraffin wax gave a coating that remained intact over the whole time period tested (5 months). However, the sulfur-paraffin system proved less efficient than sulfur alone. The most effective technique for coating was that of dipping the meshwork in solutions of sulfur in volatile solvents. Carbon disulfide containing 40% sulfur was successfully used to give good sulfur penetration of the cotton cord and allowed an attachment of about 3 parts sulfur to 1 part cotton net by weight. The surface area of the coated sulfur was estimated at about 0.1 m^2/g. No extensive effort was made to increase the exposed reactive surface area.

Sulfur coated cotton mesh was tested for its effectiveness in gettering both organic and inorganic mercury. Preliminary analytical results indicated that sulfur deployed in this form is considerably more effective as a getter of ionic mercury than was found in the original screening test results using high density sulfur tablets. Part of the improvement was traced to the gettering action of the cotton string. As illustrated in Figure 4, the cotton string sorbs mercury more rapidly than sulfur resulting in an anomalously high initial gettering rate. However, the string soon reaches an early saturation point while sulfur continues to getter mercury long after.

The data illustrated in Figure 4 were taken on a system of sulfur coated cotton net deployed on a silt clay sediment with a simulated 200 ppm mercury contamination level (as Hg^{++} from $HgCl_2$). The sediment was described in Section IV and in Figure 1. The coated net (75% sulfur) has 3/4 inch square openings and weighed approximately 0.1 pound per square foot. As the data show, the coated meshwork gettered about 0.05

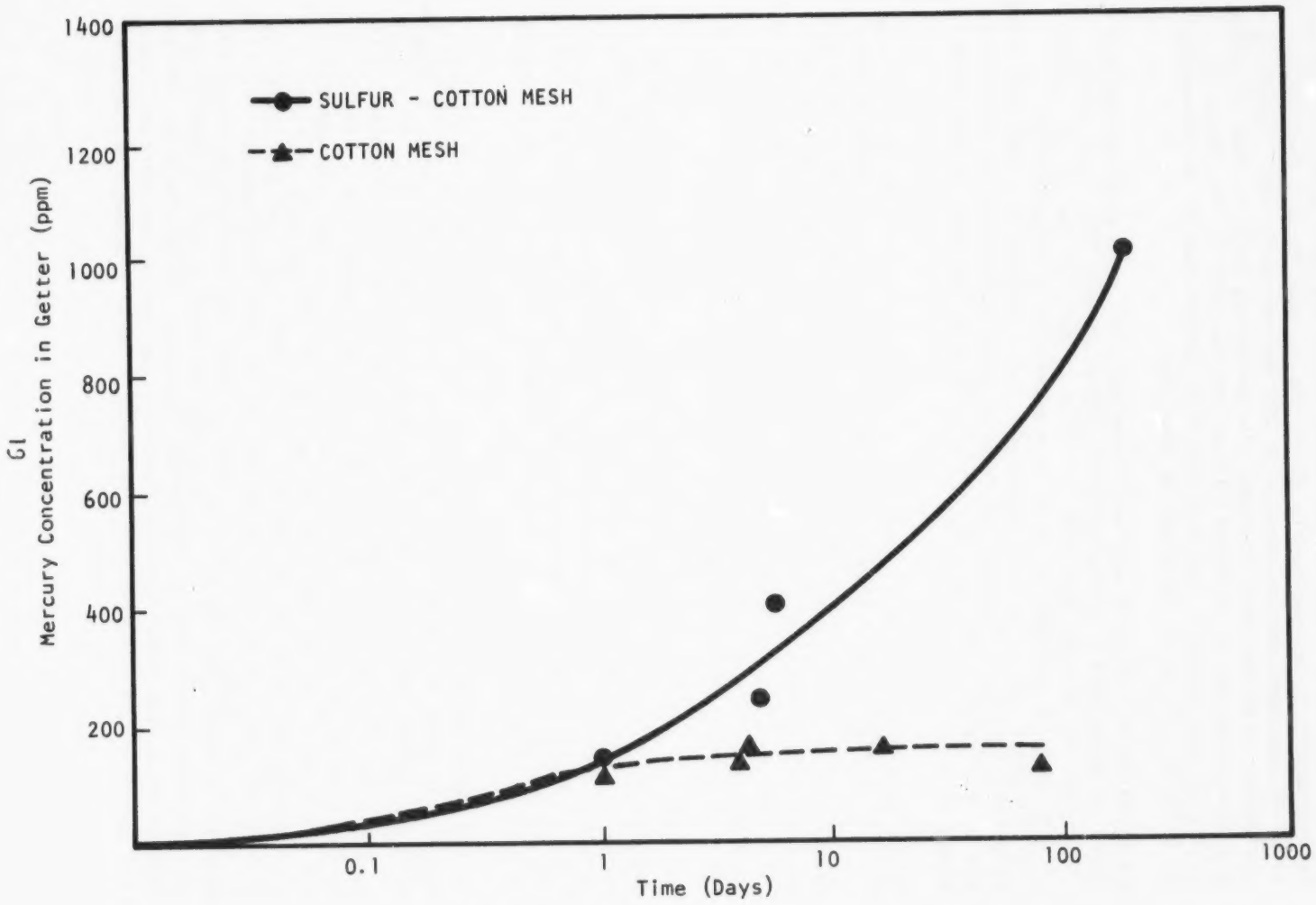

FIGURE 4 GETTER ACCUMULATION OF MERCURY

gram of mercury per square foot after being deployed 3 months. This is equivalent to approximately 2% of the mercury in a 2 inch thick layer of sediment contaminated with 200 ppm mercuric ion. Covering the getter with sediment improves the gettering rate in that it affects the concentration of desorbed (dissolved) mercury in the reaction sphere of the getter. For low levels of contamination an improvement by a factor of two or more may be expected.

Experiments on the same sediment type but with only a 25 ppm mercury level demonstrated a gettering rate approximately 100 times slower than that for the 200 ppm sample. This is because the concentration of desorbed (dissolved) mercury in the overlying water column is approximately two orders of magnitude lower (Figure 1). The non-linear rate effect results because the two sediment contamination conditions lie on different sides of the sorption-desorption equilibrium curve breakpoint.

These data were for quiet aquaria. In any real test environment, the effect of stream current on the concentration of water borne mercury will be an important consideration. However, it should be remembered that mercury tends to collect in the low density humus fraction and particularly on the "fines". Both fractions settle to form stream and lake beds only in low energy, e.g., low stream current, locations. In other words, the areas in which mercury will accumulate are those which favor the mode of operation of this getter system.

The data on short term gettering of metallic mercury was even more dramatic (Table 1). In only 3 days the sulfur accumulated 150 ppm mercury. Unfortunately, no long term experiments were conducted. Metallic mercury (Hg°) obviously is far more reactive and thus more easily removed from the sediments than the ionic mercury. In addition the oxidation of Hg° to the Hg^{++} was reduced 100-fold by the presence of sulfur (Table 2).

In the reducing environment present in most organic laden sediments, mercury is usually immobilized as either the free metal or as a complex with the humus fraction. Based on the data presented here, this reducing environment optimizes the mercury gettering action of elemental sulfur coated onto a recoverable cotton net. Mercury metal, Hg°, reacts faster with sulfur than either ionic or organic forms. In addition, the presence of sulfur retards conversion of the mercury to other more mobile and more lethal forms. It is expected that the gettering rate of Hg° will be a function of sulfur surface area because the free metal has limited solubility in water. Doubling the effective sulfur reaction surface such as by using a smaller mesh or by increasing the surface area should double the gettering rate. Unfortunately, ionic mercury is a more complicated situation. Gettering the mercuric ion from sediments is favored once the mercury level exceeds the limiting

TABLE 1 - ACCUMULATION OF METALLIC MERCURY BY SULFUR

Concentration of Mercury in Getter (ppm)	Gettering Time
2	6 hours
12	16 hours
56	48 hours
150	72 hours

TABLE 2 - EQUILIBRIUM WATER PHASE MERCURY CONCENTRATION RANGE ABOVE METALLIC MERCURY LADEN SEDIMENTS (ppm)

Mercury Form	Sulfur Coated Cotton Mesh Present	No Getter Present
Hg°	0.01 - 0.03	0.03 - 0.3
Hg^{+2}	below 0.03	~0.3

level as defined by the sediment physical and mineralogical nature. Below that point, the horizontal asymptote of Figure 1, gettering action for mercuric ion is quite slow. The humic fraction complex is very strong and the desorption and diffusion of the mercuric ion into the reaction sphere of the getter is slow. For this reason no real precision is possible in the specification of getter efficiency on sediments containing oxidized mercury; the mercury equilibrium between sediment and overlying water column must be known.

Since most contaminated sediments are reducing in nature, it is recommended that a sulfur coated cotton mesh be field tested in order to fully evaluate its potential.

Polyvinyl Alcohol Gel Getter Systems

Optimization of the reaction rate of certain getters requires a pH outside the normal range of natural waters. Although adjusting the pH in streams and lakes might be achieved chemically, this would create an ecological disaster as well as be quite impractical. Advanced Technology Center, Inc. has developed an aqueous gel of adjustable pH which might offer a unique solution to the problem of pH control. The gel is formed from polyvinyl alcohol (PVA) crosslinked with borate ion. By incorporating the getter into such a gel it is possible to control the reaction environment and thus optimize the getter's effectiveness. Of particular interest were acidified media containing elemental sulfur as one example and a sulfide forming thio-organic compound as another. The theoretical efficiency of such systems range up to a few grams of gettered mercury per gram of dry getter. PVA-getter systems of sulfur (PVA-S) and phenyl thiourea (PVA-PTU) were both found to rapidly remove both organic and inorganic mercury from highly contaminated water and sediments (Table 3).

The getter-gel system is prepared by: 1. dissolving polyvinyl alcohol in hot water; 2. blending the getter, e.g., sulfur, into the polyvinyl alcohol solution; and 3. pouring the mixture into a borax solution acidified to pH 5 with hydrochloric acid where it then coagulates. By dipping a cotton net first into the borax solution and then the PVA-getter mixture, a meshwork coated with the PVA-getter system was obtained.

Generally, 7% solutions of Du Pont Elvanol 72-60,a fully hydrolyzed, high molecular weight, polyvinyl alcohol were used. The getter, either powdered sulfur or thio-organic compound, was then dispersed in the PVA solution. The dispersion of getter in PVA solution was then coagulated with a 5% solution of either borax or ammonium pentaborate depending upon the desired pH of the gel. The use of borax as a gelling agent will produce a PVA-getter system having a pH of 10 which may be reduced to pH 5, if desired, by the addition of selected amounts of mineral acids. Ammonium

TABLE 3 - MERCURY ACCUMULATION BY GETTERS DISPERSED IN POLYVINYL ALCOHOL GEL

Mercury Type	Sediment Mercury Level (ppm)	Sediment Description	Dispersed Getter	Mercury Uptake by Getter System (ppm)			
			Deployment Time (Days)	$\frac{1}{4}$	2	5	7
$HgCl_2$	32	Silt-Clay 10% Organic Matter	Sulfur	ND*	ND		
			Phenyl Thiourea		0.4		2
$HgCl_2$	14	Silt-Clay 3% Organic Matter	Sulfur		ND		ND
			Phenyl Thiourea		ND		ND
$HgCl_2$	25	Silt-Clay 3% Organic Matter	Sulfur	ND	0.5		0.4
			Phenyl Thiourea	ND	ND		
$HgCl_2$	200	Silt-Clay 3% Organic Matter	Sulfur	50	172	682	
			Phenyl Thiourea	113	99	229	
Hg°	Bulk Mercury	---	Sulfur	2	56		
			Phenyl Thiourea	12	25		

*ND - Not Detectable

pentaborate when used as a gelling agent will produce a PVA-getter system of pH 6.5 to 7.5.

As the early experimental work proceeded it became evident that acidified gels were not stable. Furthermore, gels containing dispersed getters often dissolved in a matter of a few days. Alkaline gels coated on cotton mesh survived longer and life times up to several months were achieved in certain instances. In spite of the instability, PVA gels are worthy of additional discussion and study.

As discussed earlier, for every sediment contamination level there is a corresponding water-sediment mercury partition coefficient. PVA gels containing getters exhibit a synergistic effect in that low molecular weight polyvinyl alcohol fractions cause the equilibrium to shift in a manner to desorb mercury from the sediment. Thus, the effective concentration of mercury in the vicinity of the getter is increased resulting in a subsequent improvement in gettering rate. A number of PVA systems were tested but the majority of the study was devoted to those containing either dispersed sulfur or phenyl thiourea. In highly contaminated sediments and waters the PVA-phenyl thiourea getter rapidly collects all forms of mercury while the PVA-sulfur activity appears limited to inorganic mercury (Table 4).

Of particular significance was the removal of methyl mercuric chloride, one of the "methyl mercury" species formed in stream and lake sediments by bacterial action. Because methylated mercury is a far greater ecological hazard than its predecessor inorganic forms, the rapid gettering of this species is quite significant. Phenyl thiourea dispersed in polyvinyl alcohol was the only getter system found to be effective for methyl mercuric chloride removal in the contamination range studied. As Table 4 illustrates, the PVA-PTU gettered significant amounts of mercury even within the first few hours of deployment. Unfortunately, PVA-PTU gels were not sufficiently stable for long term studies. The effective gettering of that toxic organometallic mercury form warrants further study to develop a gel sufficiently stable to be deployed for an extended period so that the system can be field tested.

TABLE 4 - GETTERING OF METHYL MERCURIC CHLORIDE (CH_3HgCl)

CH_3HgCl Level in Overlying Water Column (ppm)	Getter Description	Accumulation of Mercury in Deployed Getter (ppm)				
	Deployment Time (days)	1	2	7	11	100
10	Phenyl Thiourea Dispersed in Polyvinyl Alcohol Gel		22			
1	Phenyl Thiourea Dispersed in Polyvinyl Alcohol Gel	3				
10	Elemental Sulfur			ND*		0.8
10	Paraffin		0.1	0.6	0.7	
10	Sulfur Dispersed in Paraffin		0.5	0.6	0.4	0.4

*ND - Not Detectable

SECTION VII

OTHER GETTER SYSTEMS

During the course of this study, it became obvious that many natural products act as mercury getters. In fact, many man-made polymeric materials also exhibit a strong but usually short-lived mercury gettering action. Previous descriptions have been devoted to the more promising getters; this section covers other systems tested but found unattractive for this applicaton.

Paraffin and Sulfur Dispersed in Paraffin

Laboratory studies at Advanced Technology Center, Inc., as well as other reports of the affinity of hydrocarbons for certain forms of mercury suggested that paraffin might be a particularly suitable getter for methyl mercuric chloride. Some rapid gettering was observed but long-term studies indicated that this was apparently a surface phenomenon of limited value (Table 4). The paraffin-sulfur type getter produced similar results for methyl mercuric chloride but more positive gettering of inorganic mercury was observed. However, the mesh coated just with sulfur was approximately 50 times more effective than the paraffin-sulfur mixtures.

Sulfur Tablets

High density sulfur tablets were found to getter metallic mercury. However, the reaction rate was proportional to surface area and the sulfur coated cotton meshworks were more effective. Similar results were observed in the gettering of mercuric ion. Approximately 1 microgram of mercury per square centimeter of surface was gettered over a 120 day period. The sulfur tablets had little effect on methyl mercuric chloride contamination, gettering less than 0.1 microgram mercury per square centimeter of exposed surface over a 120 day period.

Cotton and Paper

As previously mentioned, cotton meshwork was found to getter mercury. Levels of several hundred ppm have been reached after a few days exposure to high mercury contamination. However, the gettered mercury is less tightly bound than that held by humic materials and is subject to being resorbed by the sediments. Cotton mesh offers promise on a short-term basis but is not theoretically capable of removing mercury

to as low a level as can be achieved with mercury sulfide forming getters. As expected, paper cellulose performed similarly, however, its mercury capacity was about one-half that of cotton mesh under the same conditions.

Plastics

An interesting phenomenon observed in the laboratory was that mercury will plate out on well-cleaned plastic items on a short term basis. These include polyethylene and polypropylene laboratory ware normally regarded as inert. The process appears to be adsorption to active sites on the plastic surface. However, these sites desorb the mercury within a few days and from then on appear to be inactive. For this reason plating out is probably a better term than gettering. The total quantity of mercury temporarily adsorbed by polyethylene and polypropylene was usually less than 1 microgram mercury per square centimeter of surface. Still, high surface area yarns may offer possibilities in certain situations where short-term reusable getters are desired.

Paraffin-Thiourea

Thiourea dispersed in paraffin was also evaluated as a mercury getter. Thiourea had a strong tendency to diffuse out of the paraffin and react with the mercury away from the recoverable paraffin matrix. The sulfide settled out on the sediment thus rendering it harmless but unrecoverable. The results indicated that a less soluble thiourea derivative might be applicable. The phenyl thiourea study already described confirmed that conclusion.

Polyvinyl Alcohol-Cystine

Cystine ($C_6H_{12}N_2O_4S_2$), a naturally occurring amino-acid containing a reactive disulfide group, was dispersed in polyvinyl alcohol gel and evaluated as a mercury getter. The gettering action exhibited by phenyl thiourea was considerably greater than that of cystine.

Iron Oxides

Micro-crystalline iron oxides were evaluated for use as mercury getters, however, no significant mercury reduction in the aqueous phase was observed.

SECTION VIII

DISPOSAL OF RECOVERED MERCURY GETTER SYSTEMS

Subsequent to the recovery of the sulfur coated nets and gettered mercury, means of safe storage and disposal must be found. For short-term storage and transportation, steel barrels would be adequate. To accomplish permanent disposal two alternatives are apparent: (1) the material being in an essentially insoluble sulfide form could be buried in a dry, preferably alkaline environment, or (2) because mercury sulfide is the principal ore of mercury it should be acceptable by some mercury smelters, therefore, offering the possibility of partially defraying the cost of mercury removal from stream and lake sediments.

The economics of disposal techniques are expected to vary with geographic location, thus dollar estimates would need to be established on a regional basis.

SECTION IX

ACKNOWLEDGMENTS

The support of this project by the Environmental Protection Agency and the help provided by Dr. Curtis C. Harlin, Jr., and Dr. William R. Duffer, the Project Officer, are gratefully acknowledged.

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SECTION X

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SECTION XI

APPENDIX A

RESEARCH-DEMONSTRATION TEST PLAN

This research-demonstration test plan is designed to evaluate a sulfur coated cotton mesh mercury getter system under field conditions and to obtain the necessary research data to proceed from laboratory demonstration studies to a fully operational system suitable to broad scale application. Advanced Technology Center, Inc. (ATC) recommends that a site of approximately 1 acre (43,560 ft^2) be selected in order to fully evaluate all aspects of the system. While the areal extent of the test site may be either increased or decreased, subject to the requirements of the Environmental Protection Agency, it should be noted that a linear relationship in prices does not exist. Therefore, doubling the test area will not double the cost nor would reducing the test area by a half reduce the cost by half.

Site Selection

The geographic location and the physical parameters of the test site are not critical factors in determining the effectiveness of the system, however, they do affect costs. It is therefore recommended that both site accessibility and water depth be given careful consideration. For example, an easily accessible site having a water depth on the order of a few feet would probably eliminate the necessity of net deployment and recovery from a surface craft thus reducing cost without loss in test data reliability. Deployment in deep waters would probably increase the costs slightly. Ideally, the selected site would have a sediment contamination level over 25 ppm Hg for rapid demonstration of gettering rate and efficiency. The nature of the sediments is not critical so long as the sediment is unobstructed for getter deployment. Many sites of mercury contamination have been identified which should be applicable as a field test site. Well-publicized zones of contamination are the St. Clair and Detroit Rivers in Michigan, Lavaca Bay on the Gulf of Mexico and Bellingham Bay in Puget Sound. Many other contamination sites, as identified by the U.S. Geological Survey in Circular 643, might also be considered in the selection of demonstration sites.

Site Evaluation

Following site selection, a sufficient number of both water and bottom sediment samples to characterize the area should be obtained prior to meshwork emplacement. ATC recommends that a grid network be established

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at the test site and sampled on 50-foot centers. Both water and sediment samples should be obtained and analyzed to determine pH, dissolved oxygen, organic content, both dissolved and total mercury, and sulfide fraction. Depending on the site, sedimentation data may also be necessary.

Getter System Emplacement and Recovery

The preparation of a sufficient quantity of sulfur coated cotton netting to cover the test area will be accomplished by Advanced Technology Center, Inc.,personnel at a company facility and transported to the designated test site.

For evaluation purposes ATC recommends the use of a Number 9 Medium Cotton Netting, 1-1/2 inch stretch mesh (3/4 inch squares). To cover the test site it is estimated that 1000 pounds of net will be required. Considering the coating ratio of 3 parts sulfur to 1 part netting, approximately 3000 pounds of sulfur will be required along with the necessary solvent medium for coating.

Mode of emplacement is dependent upon site configuration. If a large waterway and deep waters are encountered, a boat of approximately 20-30 feet length will be needed. In the event of a site location having sufficient shore line accessibility the boat requirement may not exist. The coated meshwork will be deployed in 12-foot strips fastened together in shallow water to assure full coverage. Deep water coverage will be assured by net overlap when clipping adjacent strips is not practical.

The sulfur coated meshwork will remain in place for a period of six months. The test site will be sampled monthly and the previously mentioned parameters measured. Net samples will also be obtained and tested for mercury uptake and examined to determine if there has been any net deterioration or microbiological growth. Following field evaluation of the getter system the sulfur coated netting will be recovered and stored in adequate containers prior to final disposal.

Alternative Evaluation Method

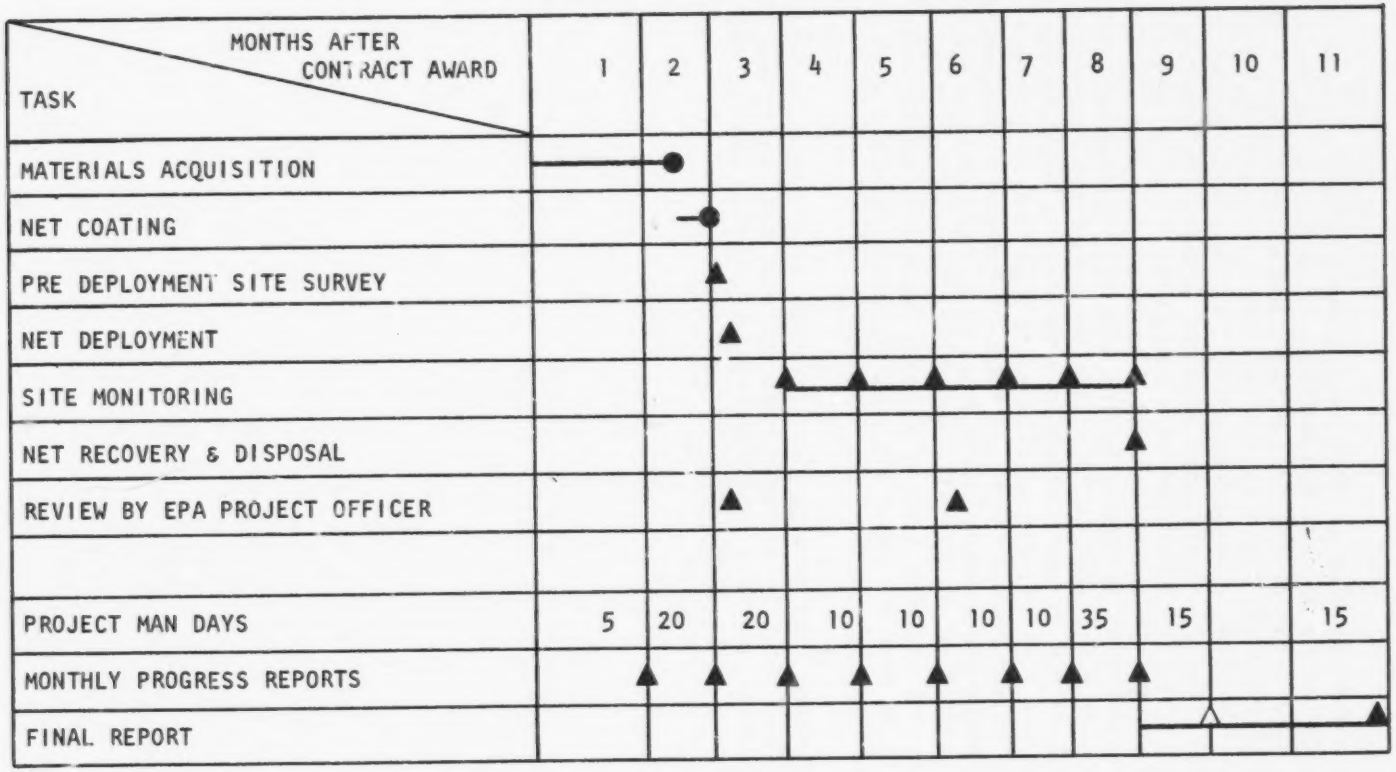
Many sites of mercury contamination exist in the United States. However, two major non-technical problems are encountered in the selection of a research field test site. First, there is almost always a problem of multiple jurisdiction over any public waterway, e.g., County and State Health and/or Water Quality and/or Water Development Boards. Even though the ATC mercury gettering system is safe and will improve water and sediment condition without any danger of water quality degradation, it may still be impossible to acquire full permission to perform the field

test. A second problem is that announcement of any mercury contamination in any site new or already documented will certainly rekindle public hysteria regardless of the test purpose and effectiveness. Therefore, as an alternative to field test under "natural" conditions, it is recommended that a simulated artificial reservoir having a surface of several thousand square feet be constructed. The reservoir would be fully lined in order to prevent contamination of ground water supplies in the area. It is estimated that a depth of two feet would be sufficient. A two-inch layer of sediments having a mercury contamination level of 25 ppm would be utilized to cover the bottom of the reservoir and a sufficient volume of water added to give a fluid level of one foot. The remaining one foot of reservoir capacity would serve as flood storage in the event of unexpected rains. The entire reservoir area would be completely fenced and properly marked to prevent unauthorized access. The sediments would be artificially doped with mercury to a level of 25 ppm. Both water and sediment from an already identified mercury contamination site would be used to inoculate the prepared reservoir with microbiota which would be encountered in a "natural" site.

It is estimated that reservoir preparation costs would be offset by reduced costs for site surveys, boat rentals, materials, and labor. Thus, the total cost for this alternative would be approximately the same as field test under "natural" conditions.

RESEARCH-DEMONSTRATION TEST PLAN

SCHEDULE



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MERCURY POLLUTION CONTROL IN STREAM AND LAKE SEDIMENTS

5. Report Date
6.
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7. Author(s)

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Organic fractions in sediments, exhibit a strong tendency to sorb inorganic mercury resulting in localized deposition near the contamination source. High concentrations of mercury do not exist in natural waters until the underlying sediments have reached their sorption limits or until soluble organic forms have been generated.

Mercury getters based on elemental sulfur and thio-organic compounds dispersed in recoverable matrices are capable of removing mercury from both the water column and underlying sediments. Elemental sulfur deployed as a coated meshwork was found to be the most effective means of recovering inorganic mercury. The gettering action occurs over a period of months with no apparent degradation in water quality. Furthermore, the presence of elemental sulfur retards biological methylation of mercury.

Long-term evaluation of mercury getter systems indicates that pH and dissolved oxygen are important only to the extent that they affect the concentration of desorbed mercury in the vicinity of the getter.

This report was submitted in fulfillment of Project Number 16080 HTD, Contract 68-01-0086, under the sponsorship of the Environmental Protection Agency. (Suggs-ATC, Inc.)

17a. Descriptors

Mercury Getters*, Sediments*, Natural Mercury Sorbents, Methyl Mercuric Chloride, Metallic Mercury

17b. Identifiers

Mercury Pollution Control*

17c. COWRR Field & Group 05G

18. Availability

19. Security Class. (Report)
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